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## (54) METALLIZING COATING COMPOSITIONS

- (71) We, MOBIL OIL CORPORATION, a Corporation organised under the laws of the State of New York, United States of America, of 150 East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to coating compositions, and in particular, to coating compositions containing metal flakes to enhance their reflectivity.
- Coatings of this type are known and described, for example, in United States Patents Nos. 2,839,378 and 2,941,894 in which vapor deposited aluminum is broken up and incorporated in a film forming coating vehicle. In U.S. Patent No. 2,941,894, the aluminum is used in amounts of from 0.028% to 0.15%, based on the weight of the composition. This proportion of aluminum was far smaller than was previously needed, but it was enough to produce a brilliant polychromatic finish. However, in the amounts needed to produce the desired metallic lustre, the pigmentation of the coating was partly obscured, reducing the contrast between the metallic flake and the background.
- Another problem with the known coatings is the tendency for the aluminum flakes to be attacked and dissolved away upon exposure to the elements. Where the aluminum flakes are dissolved away, the darker pigments of the coating show through so that some portions of the surface area are darkened due to corrosion while the remainder of the coating retains the aluminum flakes providing a mottled appearance.
- It has now been found that greater sparkle can be provided in these coating compositions if the aluminum is used in a smaller proportion, in the form of large, insoluble, resin-supported flakes of increased planarity. A greater proportion of the flakes reflect light in unison, thus creating more widely separated areas exhibiting increased sparkle. In this way, each flake shines more brightly and there is less masking of the pigment. In addition, the resin coating on the flakes protects the flakes near the surface against corrosion. As a consequence of this, surface mottling is minimized.
- According to the present invention, we therefore provide a coating composition comprising a film-forming coating vehicle and reflective metal flakes. The flakes each comprise a thin film of metal with a resin film on at least one side, preferably at least 0.25 microns (0.01 mil) thick. The resin film is substantially insoluble in the coating composition.
- These compositions produce thin coatings, e.g., the usual film thickness for automotive application from 0.5 to 1.12 microns (1.5—3.5 mils). It is preferred that the flakes should have a major planar dimension larger than the thickness of the film. The flakes of the invention cannot be used in the amounts previously considered necessary because they tend to protrude from the coating, particularly when the coating is of the usual thickness used for automotive application. It has been found that a pronounced glitter can be obtained using small flake proportions which do not result in the flakes protruding from the coating.
- The invention will be described with particular reference to the use of aluminum, because it is preferred from the standpoint of its availability, the ease with which it can be vapor deposited or otherwise manipulated and because of its high reflectivity in the extreme thinness under consideration. On the other hand, other metals capable of providing reflective surfaces when deposited in the thinness under consideration can also be used. Among these metals are

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silver, copper, gold, tin, nickel, chromium, palladium, platinum, rhodium, and their alloys.

While the invention is primarily directed to flakes which are supported by insoluble coatings on both sides, the coating may be present on only one side of the flake. In either event, the insoluble coating supports the film of metal when it is broken up into flakes, and this minimizes the disfigurement of the flake and provides improved corrosion resistance.

The resin-supported flakes can be produced by a process which involves depositing the metal on a substrate coated with a release layer and then coating the metal with the desired coating resin. The resin-coated metal can then be stripped off the substrate by dissolving out the release layer. It can then be broken up into flakes which have a resin coating on one side only. If a resin coating on both sides is desired, a layer of the coating resin is deposited on the release layer before the metal.

In the production of aluminum flake laminates of this type, it is convenient to employ a supporting substrate such as polyethylene terephthalate, which is coated with a soluble polymer layer release coating in order that the first resin coating can be easily stripped from it upon subsequent treatment with organic solvent. A layer of polymer of limited solubility is then applied and force dried to remove the solvent employed to apply it. The aluminum film is then applied in any convenient manner, but vapor deposition is preferred. While the thickness of the aluminum film may vary considerably as has been explained, it is convenient to deposit the aluminum in an amount such that there is approximately  $\frac{1}{8}$  pound of aluminum per 10,000 square feet (62g. per 1000 quadrat metre) of surface (about 2 millionths (0.05 micron) of an inch). A further coating of polymer layer of limited solubility is then applied, which may be the same or different from the layer on the other side of the aluminum. This top layer is then force dried forming a sandwich of two layers of relatively insoluble polymer, one on either surface of the film of metal. This sandwich is positioned on the support, retained by the release coating. The composite of support, release coating and sandwich or laminate is run through a bath of solvent (preferably acetone, which may be heated if desired) which dissolves the release coating and the sandwich comes off the support (usually with the aid of mechanical manipulation supplied by running the composite over rollers). This provides a slurry of partly broken up sandwich in organic solvent and this slurry is mixed with a stirrer to further break up the sandwich, without delamination, into flakes of desired size. Simple stirring is normally

adequate to break up the sandwich into flakes, but higher speed agitation may be used if simple stirring proves inadequate.

The substantially insoluble resins which are used for surfacing the aluminum film in order to produce the laminate are substantially insoluble in the ordinary organic solvents used to remove the laminate from the support on which it was formed and to dissolve the resins which are used in the coating composition. To illustrate these substantially insoluble resins, reference is made to copolymers containing 50—80% acrylonitrile, the balance of the copolymer being illustrated by ethyl acrylate. These copolymers are soluble in relatively strong solvents such as dimethyl formamide, but they will not dissolve in the more conventional solvents of lesser activity such as acetone. Similarly, polyvinyl butyral is relatively insoluble in aromatic solvents and ketones, and it may be dissolved and applied using alcoholic solvents. Moreover, polyethylene terephthalate is soluble in low concentration in cresylic acids and can be applied from solution in them. The acrylic polymers normally used in automotive coatings as well as the other resin systems known to be useful for such purposes, such as the alkyl resin-aminoplast resin blends disclosed in U.S. Patent No. 2,941,894, are soluble in one or more of the conventional solvents used in automotive finishes, e.g., mixtures of aromatic hydrocarbons such as xylol and aliphatic hydrocarbons, such as mineral spirits of naphtha, which may be supplemented by ketones such as methyl ethyl ketone or methyl isobutyl ketone. The resins used as a coating to surface the aluminum film on both sides thereof must therefore be substantially insoluble in these solvent systems.

One preferred composition comprises flakes which are a film of aluminum surfaced on both sides with resin films insoluble in acetone. These flakes are dispersed in a coating composition comprising aromatic hydrocarbon solvent and ketone solvent and organic film-forming resin dissolved in the solvents.

Instead of the ethyl acrylate/acrylonitrile copolymer referred to above, a 5% solution of polyvinyl butyral in a 50/50 weight ratio mixture of ethanol and butanol may be used. This deposits a film of resin on the aluminum film which does not dissolve in the aromatic and ketone solvents used to release the sandwich. This film of resin also does not dissolve in many of the solution coating compositions in which the resin supported flakes are incorporated. A 5% solution of polyethylene terephthalate in cresylic acid may also be used instead of the ethyl acrylate/acrylonitrile copolymer solution.

It should be understood that while the

resins used to coat the metal film must be insoluble in the solvent which is utilized, this does not preclude limited swelling of the resin in the solvent medium. In this respect, it will be appreciated that the resin films are not intended to prevent break-up of the released laminate into flakes and limited swelling of the resin film in the solvent medium may enhance resin break-up.

The resin is preferably applied from a solution, followed by removal of the solvent by volatilization (preferably using force drying in which heated air is blown over the wet coating to dry it). Curing conditions for a limited thermosetting cure may be used, assuming the support and the release coating can withstand the temperatures involved. Relatively strong solvents may be used for application since they are rapidly evaporated so as to avoid unduly injuring the supporting materials.

To facilitate removal of the coated metal film from the substrate, a resin which is readily soluble in the solvents under consideration is used as a release layer. For example, isobutyl methacrylate is a typical release coating which may be used. Rosin or maleinized rosin or ester gum will further illustrate soluble release layers which may be used. Thus, a laminate is formed and later physically removed from its support, using a solvent which dissolves the release coating holding the laminate on the support. The resin used to form the laminate is substantially insoluble in this solvent.

The concentration of resin in the solution helps to determine the thickness of the resin films on the metal. Since thin films are desired, low solids content solutions are preferred, e.g., 3 to 15% solids. The resinous film supporting the metal is preferably at least 0.01 mil (0.25 micron) in thickness, more preferably at least 0.08 mil (2 microns). While the metal film should generally not be so thick as to prevent break-up using an appropriate solvent and mechanical agitation, the preferred films do not exceed 0.2 mil (5 microns) in thickness.

The resin films used to coat the metal film may be dyed or pigmented to impart color to the reflected light. Similarly, the metal can be colored or anodized and the surfacing resin films can function to seal the color on the metal. Numerous decorative effects will be apparent from this capacity to vary the color and appearance of the flakes which are used.

Although vapor deposition is the preferred method for forming the thin aluminum film, other methods may also be used, for example, electroless deposition, and as long as the aluminum film is sufficiently thick to reflect light, it can be used. Electroless deposition is illustrated by the decomposition of aluminum hydride as described in U.S.

Patent No. 3,462,288. The upper limit of film thickness is not critical, but is of the order of 20–30 millionths of an inch (0.5 to 0.75 micron), though subject to variation depending on the metal selected and economic factors. More particularly, the thickness of the metal film is normally from 0.5 to 25 millionth of an inch (0.01 to 0.6 micron), preferably from 0.5 to 5 millionths of an inch (0.01 to 0.1 micron). Various methods for producing such films are described in the patents referred to previously. The thinnest aluminum films having a thickness of less than 3 millionths of an inch (0.07 micron) are especially benefited because in the absence of the resin support, they are more easily distorted by the agitation used to break the film into flakes. Also, these thinner films have less mass and would corrode more easily at the surface to produce a mottled appearance upon exterior exposure were it not for the resin coating. Further, the combination of thin metal film and insoluble resin coating minimizes settling of the flakes in the coating composition.

When the laminate is agitated in a liquid medium comprising an organic solvent system which is not capable of dissolving the resin on the film, the laminated form is retained as the film is broken up. The thin resin films do not prevent break-up into the desired flakes, but they protect the flakes during break-up and cause the production of flakes which are more planar than those previously produced. Without the supporting resin films, the flakes at 600 magnification are significantly warped, e.g., they undulate or have curled edges and are wrinkled. This reduced planarity minimizes the proportion of the flake which can reflect light from a given source into the eye of a viewer. It is preferred to use flakes having their largest planar dimension in the range of 30 microns, preferably in excess of 60 microns, to 200 microns. It is especially preferred to employ flakes which have a planar dimension larger than the thickness of the coating which is formed. As a result, the flakes in the film are able to reflect the light over a relatively large surface area of the flake to provide a pronounced glitter which is especially useful when there are less than 100 reflecting flakes per 5.5 square millimeters of coating, so that the glittering flakes may be widely spaced. In this way the coating sparkles in the light as opposed to providing a more generalized metallic lustre of reduced intensity accompanied by a partial masking of the coating pigmentation.

The agitation is preferably continued until about 95% by weight of the flakes have a major dimension in the range of 30–80 microns.

The resin supported metal flakes must be employed in very small amounts, the pre-

ferred proportions being below the minimum proportion of 0.028% aluminum specified in U.S. Patent No. 2,941,894. The preferred proportions in the present invention are from 0.0005% to 0.025% of aluminum, based on the weight of the composition. Even smaller proportions of aluminum on the same basis can be used down to 0.0003 weight per cent. In certain instances when the pigmentation is denser or more darkly colored, it may be desirable to increase the proportion of aluminum, above the preferred maximum but such cases will be rare. The maximum proportion which can be tolerated is 0.035 weight per cent. If the weight proportion of aluminum used in the present invention is increased beyond this upper limit, the particles tend to protrude from the coated surface. Accordingly, the weight proportions of metal in the flakes should be limited to avoid the protrusion.

The resin supported metal flakes are dispersed in a film-forming coating vehicle. The coatings are particularly useful as topcoats for the exteriors of automobiles. For this purpose, acrylic coatings are of special interest. They are illustrated by solution polymers containing 80% to 100% of polymerized methyl methacrylate, any balance of the polymer being monoethylenically unsaturated monomer which is copolymerizable with methyl methacrylate for example, other alkyl esters of acrylic or methacrylic acid such as butyl acrylate. Small amounts of acrylic or methacrylic acid may be present if desired. While acrylic polymers of the type used in automotive finishes are particularly preferred, any lacquer, or coating polymer system, or enamel, may be used whether clear or pigmented. The latter are especially useful, particularly in the high gloss coating systems which are used for automobile topcoats. These finishes frequently include cellulosic materials such as cellulose acetate butyrate and appropriate plasticizers. Typical acrylic automobile finishes which may be used are described in United States Patent No. 2,849,409. The patents referred to earlier also disclose coating vehicles which may be used.

The metal laminate flakes may be used in aqueous coating compositions. Normally, the highly reactive aluminum flakes cannot be used in normally alkaline water medium because the aluminum will react with the water. In this invention, the aluminum is protected so that the aluminum particles may be incorporated in an aqueous coating system without ill effect. In this case the aluminum laminate is stripped from the supporting layer using a water miscible organic solvent and the dispersion of aluminum flake in the solvent is then dispersed in the aqueous coating composition.

The resin-supported metal flakes are in-

sulated from one another and, as a result, the coating compositions can be subjected to a high voltage electrostatic charge without arcing. This has significance in the automobile industry where electrostatic coating processes are frequently used. The compositions of the invention may even be atomized electrostatically as part of the electrostatic coating process.

The slurry of resin-supported aluminum flakes is dispersed in the selected coating composition in an amount to provide the desired metal content. The metal content of the final metallizing coating composition is preferably 0.01% by weight.

While the coating composition itself is subject to considerable variation, a preferred coating composition is illustrated by combining 50 parts of a methyl methacrylate copolymer with 30 parts of a polyester plasticizer and 20 parts of cellulose acetate butyrate, the solvents being aromatic hydrocarbons and ketones (parts are parts by weight). A preferred methyl methacrylate copolymer contains 92% of methyl methacrylate and 8% of isobutyl acrylate and is supplied as a 40% solids solution in a 3/1 blend of toluol and methyl ethyl ketone. An appropriate polyester plasticizer contains 37.7% neopentyl glycol; 22.9% pelargonic acid; 21.0% isophthalic acid; and 18.4% adipic acid. This polyester is supplied as a 95% solids solution in xylene. The cellulose acetate butyrate is used as a 25% solids solution in toluol and acetone.

By mixing the three solutions in the form recited, a preferred coating vehicle is obtained. If desired, a small proportion of the methyl methacrylate copolymer (2% by weight) may be replaced by another methyl methacrylate copolymer providing increased adhesion, e.g., a copolymer containing 79% methyl methacrylate; 8% isobutyl acrylate; 8% methacrylic acid; and 5% of any conventional adhesion promoting agent. For example, the methacrylic acid can be reacted with propylene imine. Another known variation is to replace the methacrylic acid with glycidyl methacrylate which may be aminated or ammoniated as desired. Still another known variation is to replace the methacrylic acid with an amino acrylate. All of these and other similar expedients are well known to enhance the adhesion of a methacrylate coating system to a substrate base and may be used if desired.

The solvent system for the methacrylate polymer containing the adhesion promoting agent can be the same as that used for the methyl methacrylate polymer which does not contain the adhesion promoter.

The coating composition may be used clear, but it is preferred to pigment it. The pigment may be dispersed in the coating composition to provide the background color

for the reflective aluminum flakes. Appropriate pigments for coating compositions are well known, the pigments more usually employed in the formation of automotive coatings including carbon black, phthalocyanine green, phthalocyanine blue, ferrite yellow, red iron oxide, titanium dioxide, iron blue, chromium tetrahydrate, lead chromate and indanthrone blue. Numerous other pigments may also be used. On the other hand, and while pigmentation is normally present, the supported metal flakes can be employed in clear coatings, especially when they are deposited on top of a previously applied pigmented coating.

Although the coatings of the present invention contain fewer metal flakes than were previously needed to produce a pronounced metallic glitter, the sparkle of the coating is greater than before because each flake provides more glitter. Further, with less flakes in the coating, the background pigmentation is not obscured and the contrast between the glittering flakes and the background is increased.

The invention is illustrated by the following Example:—

A support layer of polyethylene terephthalate film 0.69 mil (7.5 microns) thick is first surfaced with a release coating of polyisobutyl methacrylate. If desired, a copolymer of methyl methacrylate and isobutyl acrylate in a weight ratio of 92/8 or a maleic modified ester gum or rosin or gelatin may be used instead of the polyisobutyl methacrylate.

After the release coating has been dried, a 0.10—0.15 mil (2.5—3.7 micron) thick film of a copolymer of 40% ethyl acrylate and 60% acrylonitrile is deposited over it (percentages are by weight). This copolymer may be made by copolymerizing the monomers at 25% solids in solution in dimethyl formamide in the presence of 1% benzoyl peroxide catalyst, the reaction being carried out at reflux for 8 hours. The solution of resin so-obtained is then diluted with additional dimethyl formamide to a viscosity enabling roll coat application. The coating is then force dried.

After drying, the layer of ethyl acrylate/acrylonitrile copolymer is surfaced with a vapor deposited aluminum film weighing  $\frac{1}{8}$  pound per 10,000 square feet (62 g. per 1000 quadratmeter). A top layer of the same ethyl acrylate/acrylonitrile copolymer is then applied to the exposed aluminum film surface, as by roll coating, in a thickness of 0.10—0.15 mil (2.5—3.7 micron).

The result is a composite which can be removed by running it through an organic solvent (acetone) with the composite being run under and over rolls or bars to help the resin-coated aluminum film sandwich to separate from the support. Ordinary agita-

tion can then be used to reduce the supported aluminum flakes to desired size.

The slurry of aluminum flakes in acetone is broken up by agitation so that about 95% by weight of the metal is in the form of flakes having their largest planar dimension in the range of 30—80 microns. This slurry is then incorporated in the paint in an amount to provide 0.01% by weight of aluminum based on the weight of the paint. The paint is constituted by the mixture of three solutions described above (methyl methacrylate polymer: polyester: cellulose acetate butyrate, 50:30:20). This mixture is pigmented by the incorporation of 2.3 parts of phthalocyanine green pigment and 0.5 part of ferrite yellow pigment per 100 parts of paint. This provides a green automotive metallic lacquer which, when sprayed on primed metal and baked to remove the solvent, will deposit a high gloss finish having a thickness of 1—2 mils (0.25—0.5 micron) and containing less than 100 metal flakes per 5.5 square millimetres of coating which are near the exposed surface and, therefore, highly reflective. The coating exhibits great sparkle and glitter in the light, despite the small amount of aluminum in the flakes which are present.

#### WHAT WE CLAIM IS:—

1. A coating composition comprising a film-forming coating vehicle, and resin-supported reflective metal flakes in an amount of from 0.0003% to 0.035% of metal, based on the weight of the composition, the flakes comprising a thin film of metal surfaced on at least one side with a resinous film, the resin of the film being substantially insoluble in the coating composition.
2. A coating composition according to claim 1 in which the metal is aluminum.
3. A coating composition according to claim 2 in which the aluminum film is vapor-deposited aluminum.
4. A coating composition according to any of claims 1 to 3, wherein the resinous film has a thickness of at least 0.25 micron (0.01 mil).
5. A coating composition according to any of claims 1 to 4 in which the flakes have a planar dimension of at least 30 microns.
6. A coating composition according to claim 5 in which the flakes have their largest planar dimension in the range of from 30 to 200 microns and the aluminum film has a thickness of less than 0.07 micron (31 millionths of an inch).
7. A coating composition according to any of claims 1 to 6 in which the substantially insoluble resin films on the metal have a thickness of at least 2 microns (0.08 mil).
8. A coating composition according to any of claims 1 to 7 in which the metal flakes are coated on both sides with the resin.

9. A coating composition according to any of claims 1 to 8 in which the flakes are present in an amount of from 0.0005% to 0.025%, based on the weight of the composition. 20
10. A coating composition according to any of claims 1 to 9 in which the metal film of the flakes has a thickness of from 0.01 to 0.1 micron (0.5 to 5 millionths of an inch). 25
11. A coating composition according to any of claims 1 to 10 in which the flakes comprise a film of aluminum surfaced on both sides with resin films insoluble in acetone, and the flakes are dispersed in a coating composition comprising aromatic hydrocarbon solvent and ketone solvent and organic film-forming resin dissolved in the solvents. 30
12. A coating composition according to claim 11 in which the film-forming resin comprises a solution polymer containing at least 80% of polymerized methyl methacrylate. 25
13. A coating composition according to any of claims 1 to 10 which is an aqueous coating composition. 25
14. A coating composition comprising a film-forming vehicle and resin-coated metal flakes according to claim 1 and substantially as herein described. 30

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